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NITROGEN-PHOSPHORUS POLYMERS

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FOREWORD

This report was prepared by the Anorganisch-Chemisches Institut, University of Heidelberg, Heidelberg, Germany under Contract AF 61(052)-682. This report was initiated under Project No. 7342, "Fundamental Research on Macromolecular Materials and Lubrication Phenomena", Task No. 734201, "Basic Factors on the Synthesis of Macromolecular Material". The work was administered under the direction of the Air Force Materials Laboratory, Research and Technology Division with Dr. W. L. Lehn acting as project engineer.

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This technical report has been reviewed and is approved.

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ABSTRACT

A variety of chemical systems containing phosphorus-nitrogen bonds have been investigated as potential intermediates for the synthesis of polymeric materials having extreme thermal and chemical stability. These investigations include: the preparation of various phosphorus nitride salts containing phenyl groups and the reactions of these compounds with diamines in order to produce phosphorus-nitrogen polymers, the preparation of various phosphorus nitride dichlorides in order to obtain suitable starting materials for isomer preparation and the reaction of known phosphorus nitride dichlorides in such a manner as to form six- and eight-membered ring systems containing phosphorus and nitrogen as ring components which would be linked by $N-SO_2-N$ bridges.

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INTRODUCTION

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Section III Further Reaction of These Compounds with Diamines in the Attempt to Produce Phosphorus-Nitrogen Polymers.

Section IV The Preparation of Various Phosphorus Nitride Dichlorides in Order to Obtain Suitable Starting Materials for Preparing Isomers.

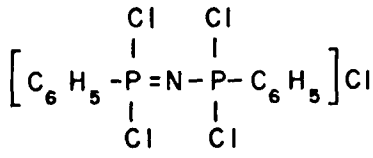
Section V Reaction of Known Phosphorus Nitride Dichlorides in Such a Manner as to Form Six- and Eight-Membered Ring Systems Containing Phosphorus and Nitrogen as Ring Components and Which Would be Linked by Way of $N-SO_2-N$ Bridges.

Section VI Other Attempts to Prepare Polymeric Phosphorus Nitrogen Compounds.

SECTION II

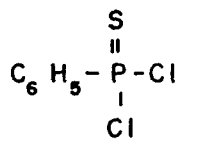
THE PREPARATION OF VARIOUS PHOSPHORUS NITRIDE SALTS CONTAINING PHENYL GROUPS

The first attempt was to prepare compound I and four different methods appeared feasible. These methods were: a) The reaction between phenylphosphorus dichloride, $C_6H_5PCl_2$, and S_4N_4; b) The reaction between phenylphosphorus dichloride and NCl_3; c) The reaction between phenylphosphorus dichloride, PCl_5, and hydroxylammonium salts; and d) The reaction between phenylphosphorus dichloride, chlorine, and NH_4Cl. It became evident that compound I could be prepared by all of these reactions.



I

Next it was necessary to ascertain which of the described procedures was most expedient for the goal in mind. First, the reaction between tetrasulfur tetranitride S_4N_4, and $C_6H_5PCl_2$ was investigated; this was carried out in an atmosphere of nitrogen at 0-10°[6]. The mole ratio employed consisted of 1 mole S_4N_4 to 10 moles $C_6H_5PCl_2$. S_4N_4 is soluble in dichlorophenylphosphine, and a vigorous, strongly exothermic reaction sets in at once. This reaction led to several products; compounds II, III, IV, and V were obtained in addition to I.



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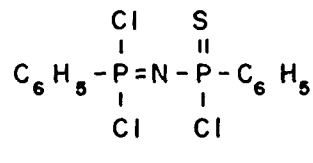

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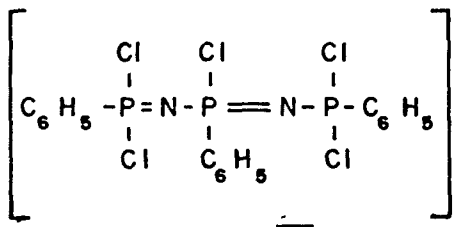

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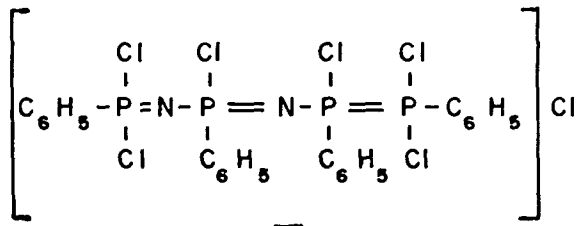


V

When the reaction mixture was cooled, compound I crystallized in colorless prisms. This substance melted at 210°C in an evacuated tube, and was readily soluble in chloroform, nitrobenzene, and nitromethane. It was insoluble in ether, benzene, and carbon tetrachloride. Cryoscopic molecular weight determination in nitrobenzene gave values only half as large as expected from theory, showing that the compound dissociates in this solvent. The electrical conductivity measured in nitromethane solution also indicated that dissociation into two ions occurs.

The P^{31} nuclear magnetic resonance (n.m.r.) spectrum of compound I showed only a single resonance peak of strong intensity with a chemical shift of -41.7 ppm referred to a

$POCl_3$ standard. However, the n. m. r. spectrum of the reaction mixture as a whole was much more complicated. A resonance signal appeared at -75.4 ppm, which is to be ascribed to compound II. Further peaks, one at -29.7 ppm and another at -15.9 ppm can be attributed to compound IV, whereas peaks at -24.8 and -9.2 ppm arise from V. Resonance peaks at -60.7 and -20.8 ppm result from compound III. As expected, only the resonance peaks arising from compounds I and II appeared as singlets.

Since the reaction between $C_6H_5PCl_2$ and S_4N_4 did not lead to a homogeneous product, it became necessary to look for better methods of preparing compound I. Therefore, the reaction between $C_6H_5PCl_2$ and NCl_3 was investigated and the following course of reaction was as follows:

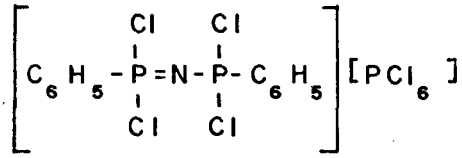
$$3\,C_6H_5PCl_2 + NCl_3 \longrightarrow (C_6H_5)_2P_2NCl_5 + C_6H_5PCl_4$$

I

According to this scheme, compound I was obtained in crystalline form in 20 percent yield.

In this procedure, 1 mole NCl_3 was reacted with 3 moles dichlorophenylphosphine in chloroform solution. The reaction was strongly exothermic. With this mole ratio, the initially yellow-green chloroform solution became bright yellow as the reaction progressed. Compound I could be precipitated as an oil from this solution by the addition of dry ether. This oil consisted principally of I, but also contained compounds IV and V.

Then experiments were conducted with an aim to preparing compound I from phenylphosphorus dichloride, PCl_5, and hydroxylammonium chloride. We found that according to the mole ratios employed, two products, namely, salts I and VI, could be obtained from the reaction of $C_6H_5PCl_2$ and PCl_5 with $[H_3NOH]Cl$. For the preparation of VI, a mole ratio of $C_6H_5PCl_2$: $[H_3NOH]Cl$: PCl_5 of 1:1:1, or better 2:2:3, is recommended. If the components are allowed to react in these proportions in an inert solvent at elevated temperature, the reaction proceeds almost quantitatively according to the following equation:



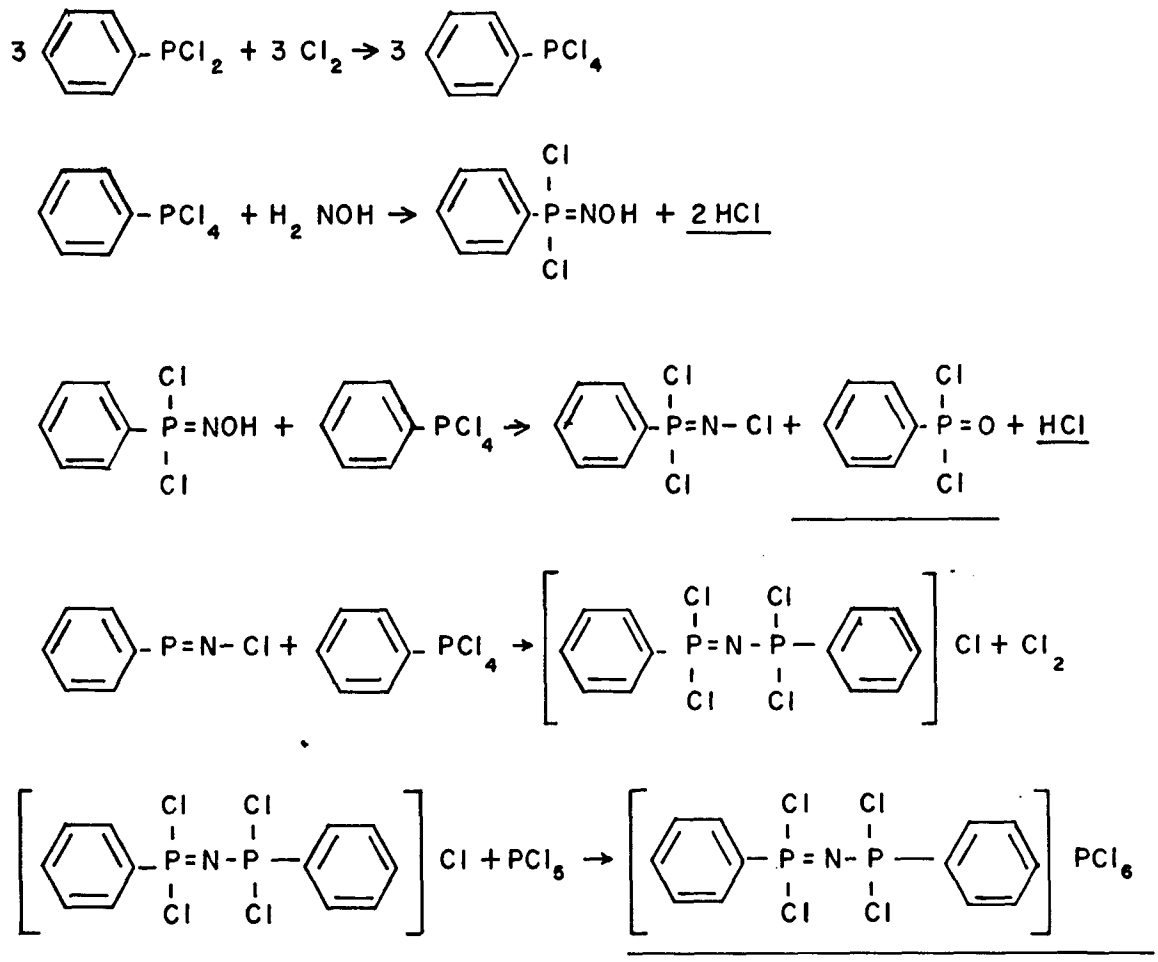
VI

$$3\,C_6H_5PCl_2 + 3\,PCl_5 + 3[H_3NOH]Cl \rightarrow \text{VI} + C_6H_5P(O)Cl_2 + 2\,HCl$$
$$+ 2\,OPCl_3 + 2\,NH_4Cl$$

The course of the reaction can be understood in terms of the following scheme:

$$2\,PCl_5 \rightleftharpoons [PCl_4]^+ + [PCl_6]^-$$

$$2\,H_3NO + 2\,PCl_5 \rightarrow 2\left[H_3N\text{-}O\text{-}PCl_4\right]^+Cl^-$$
$$\downarrow$$
$$\underline{2\,NH_3} + \underline{2\,OPCl_3} + 2\,Cl_2$$



The yield of I was somewhat inferior to that of VI when hydroxylammonium chloride, dichlorophenylphosphine, and PCl_5 were employed as starting materials. In this case, the yield is improved when more than 1 mole hydroxylamine per mole $C_6H_5PCl_2$ and PCl_5 is used. However, compound VI can be easily converted into I by slowly heating it to about 150°C in vacuo. PCl_5 is sublimed.

A description of the experimental details of the reaction is given. Each experiment was conducted in a one-liter, 3-necked flask fitted with a stirrer and a reflux condenser which was connected by means of drying tubes with an aspirator. Chloroform was employed as a solvent, but 1, 2-dichlorethane and tetrachloroethane are also suitable. A bath temperature of 130°-140°C was used. Towards the end of the reaction an aspirator vacuum was applied.

In combining the reagents, we found that it was expedient to mix first the $C_6H_5PCl_2$ with a larger portion of solvent, transfer this mixture to the flask, and then rinse in the hydroxylammonium chloride and PCl_5 with the remaining quantity of solvent. The hydroxylammonium chloride had to be dried and pulverized beforehand. The reaction usually commenced with frothing and the evolution of heat immediately following the addition of the reacting ingredients. In a few exceptional cases, the initial application of heat served to get the reaction under way more promptly. The duration of reaction was two to three hours; at the end of this time, the

evolution of HCl had ceased and a white precipitate was formed which consisted mainly of ammonium chloride and partly of unreacted $H_2NOH \cdot HCl$. The remaining bright yellow solution was filtered through a glass frit while still warm, care being taken to exclude moisture.

A. PREPARATION OF $\left[C_6H_5P(Cl_2)=N-P(Cl_2)C_6H_5 \right] \left[PCl_6 \right]$ (VI)

The reaction between $C_6H_5PCl_2$, $\left[H_3NOH\right]$ Cl, and PCl_5 is carried out in a mole ratio of 1:1:1, or better 2:2:3 respectively. The following results were obtained with 54.65 g(0.305 mole) $C_6H_5PCl_2$, 21.4 g (0.305 mole) $\left[H_3NOH \right]$ Cl, and 95.5 g (0.46 mole) PCl_5 in 400 ml of chloroform as a solvent, using a bath temperature of 150°C during the reaction:

11.65 g of residual white solid were isolated. After partial evaporation of the remaining bright yellow solution, pale yellow, lustrous crystals of the required compound VI were obtained. Yield: 40.3 g $\left[C_6H_5P(Cl_2)=N-P(Cl_2)C_6H_5\right]\left[PCl_6\right]$(VI). In addition, 51.3 g of a yellow oil were produced. This oil contained small amounts of solvent, $OPCl_3$, and $C_6H_5P(O)Cl_2$, as well as some VI together with apparently higher members of the form $\left[C_6H_5(Cl_2)P=(N-PCl_2)_n=N-P(Cl_2)C_6H_5\right]^+$. When this mixture was heated in vacuo to about 125°C (bath temperature at 150°C and higher), most of the $C_6H_5P(O)Cl_2$ could be distilled off. The residue consisted of a dark yellow viscous oil. After dry benzene had been added to this oil, two phases formed, namely, a dark yellow or brown benzene phase and a heavy, yellow oil phase from which crystals separated. The upper phase (benzene) was decanted and the yellow oil was shaken with dry ether or CCl_4, whereupon a further quantity of pale yellow crystals of the desired compound could be isolated. In this way, additional 21.5 g of compound were obtained. Total yield: 61.8 g (0.1 mole).

Analysis of the compound $P_3NCl_{10}C_{12}H_{10}$ (615.7) VI

Required: C 23.4%, H 1.63%, N 2.28%, P 15.10% Cl 57.6%

Found: C 23.22%, H 1.83%, N 2.45%, P 15.6%, Cl 56.8%

The molecular weight determination (cryoscopically in nitrobenzene) gave the value 294; this shows that the substance dissociates into two univalent ions in this solvent. The compound is very hygroscopic, and has no definite melting point. When heated in vacuum, the salt merely turns yellow and local overheating leads to decomposition of individual crystals, whereby a dark yellow oil is formed.

The following results were obtained with a run consisting of 64.5 g (0.36 mole) $C_6H_5PCl_2$, 25.2 g (0.36 mole) $H_2NOH \cdot HCl$, and 75 g (0.36 mole) PCl_5 in 500 ml of chloroform at a bath temperature of 75°C.

The amount of white residual solid was 12.4 g. 30.5 g (0.05 mole) of compound VI was isolated together with 78.4 g of yellow oil, from which 6.81 g of compound I separated out.

In a further run, 93.9 g (0.52 mole) $C_6H_5PCl_2$, 36.7 g (0.52 mole) $H_2NOH \cdot HCl$, and 109 g (0.52 mole) PCl_5 were reacted in 380 g of chloroform at a bath temperature of 135°C. Under these conditions, 21.2 g of white residual solid were produced. After most of the solvent had been removed from the bright yellow solution, 61.5 g (0.1 mole) of compound VI were obtained, together with 90.15 g of yellow oil which was not processed further.

It was established from this series of experiments that the most favorable mole ratio of $C_6H_5PCl_2$: PCl_5: $[H_3NOH]Cl$ is 1:1.5:1, under which condition VI is formed in 99 percent yield. On the other hand, the yield of VI with a mole ratio of 1:1:1 was only 57 percent. Thus an excess of PCl_5 is necessary for quantitative formation of VI.

B. THE PREPARATION OF $\left[C_6H_5P(Cl_2)=N-P(Cl_2)C_6H_5\right]Cl$ (I)

1. The synthesis of $\left[C_6H_5P(Cl_2)=N-P(Cl_2)C_6H_5\right]Cl$ (I) by heating $\left[C_6H_5P(Cl_2)=N-P(Cl_2)C_6H_5\right]PCl_6$.

When VI is heated slowly in vacuum at a bath temperature of 147°C and higher, the yellow crystals are gradually converted into a white, mealy material (I) and PCl_5 sublimes off. The conversion is practically quantitative.

2. The synthesis of $\left[C_6H_5P(Cl_2)=N-P(Cl_2)C_6H_5\right]Cl$ from $C_6H_5PCl_2$, $[H_3NOH]Cl$, and PCl_5.

The reaction between $C_6H_5PCl_2$, PCl_5, and $[H_3NOH]Cl$ in this case is carried out along the same lines as already described for VI, except that an excess of hydroxylammonium chloride is now employed. More than one mole of the latter per mole $C_6H_5PCl_2$ and PCl_5 is required if a sufficiently satisfactory yield is to be obtained.

When 59.3 g (0.33 mole) $C_6H_5PCl_2$, 79.6 g (1.14 mole) $[H_3NOH]Cl$, and 78.9 g (0.38 mole) PCl_5 (mole ratio 1:3.4:1.1 respectively) were reacted in 500 ml of chloroform at a bath temperature of up to 50°C, 70.3 g of white residual solid were produced. Only an oil, and no solid material was obtained from the remaining solution after the solvent had been removed by distillation. After $C_6H_5P(O)Cl_2$ had been distilled off from this oil in vacuo at a bath temperature of 150°C and the residue was allowed to cool, yellowish brown crystals separated. These were washed with dry benzene in order to remove the brown, oily impurities. The white solid which remained had a composition corresponding to formula I. Its melting point in vacuum was 210°C. The yield of I from this run was 11.5 g (0.028 mole).

Analysis of I:

Required: C 35.4%, H 2.48%, N 3.4%, P 15.2%, Cl 43.6%

Found: C 35.55%, H 2.58%, N 3.6%, P 15.5%, Cl 42.0%

The compound is extremely hygroscopic. It is only very sparingly soluble in benzene, and hence it can be purified by washing with this solvent.

The compound $C_6H_5\ PCl_2=N-PC_6H_5Cl(O)$ can be easily obtained from I when an excess of sulfur dioxide is condensed onto the latter at about -15°C. The following reaction then occurs:

$$\left[C_6H_5P(Cl_2)=N-P-C_6H_5(Cl_2)\right]Cl + SO_2 \rightarrow C_6H_5P(Cl_2)=N-\overset{O}{\overset{\|}{P}}(C_6H_5)Cl + OSCl_2.$$

In carrying out this reaction, the mixture is allowed to warm slowly to room temperature, after which the excess SO_2 and the thionylchloride formed are removed in vacuum. The compound is an oil, and cannot be distilled without decomposition.

When the compound $C_6H_5PCl_2{=}N{-}P(C_6H_5)Cl(O)$ is heated to about 140°C, it undergoes pyrolysis. If this process is conducted in a distillation apparatus, $C_6H_5P(O)Cl_2$ distills over slowly and the dark, viscous product remaining, which is soluble in benzene, has the composition $\left[C_6H_5P(Cl){=}N{-}\right]_n$. Hence, pyrolysis of this substance leads to polymeric phenylphosphorus nitride chloride.

Further study of feasible reactions for producing compound I showed that the following particular route was the best one:

$$C_6H_5PCl_2 + Cl_2 \rightarrow C_6H_5PCl_4$$

$$2\,C_6H_5PCl_4 + NH_4Cl \rightarrow \left[C_6H_5\overset{\displaystyle Cl\ \ Cl}{\overset{|}{P}{=}N{-}\underset{|}{P}}{-}C_6H_5\right]Cl + 4\,HCl$$

I

The most suitable procedure proved to be the following:

Phenyltetrachlorophosphine, $C_6H_5PCl_4$, is first prepared from phenyldichlorophosphine, $C_6H_5PCl_2$, by dissolving 175 g of the latter in 200 ml of tetrachloroethane and sparging in dry chlorine until the gas phase above the solution is saturated with Cl_2. It is advisable to apply cooling during this stage. 26 g NH_4Cl are then added and the mixture is heated to 160°-180°C. Following the reaction, excess ammonium chloride is filtered off and the tetrachloroethane solvent distilled in vacuum; the residual oil is treated with benzene, whereupon compound I crystallizes out. The crystals are then filtered. When sulfur dioxide gas is allowed to act upon compound I in solid form at room temperature, the following reaction takes place:

$$SO_2 + \left[C_6H_5\overset{\displaystyle Cl\ \ Cl}{\overset{|}{P}{-}N{=}\underset{|}{P}}C_6H_5\right]Cl \rightarrow OSCl_2 \qquad C{=}\overset{\displaystyle C_6H_5\ \ C_6H_5}{\overset{|}{P}{-}N{=}\underset{|}{P}}{-}Cl$$

VII

After a period of two to three hours, compound VII is obtained in almost quantitative yield. The crude product is impure and oily; it can be purified by distillation in vacuo at 210°C/0.01 mm Hg. The distillate solidifies; its melting point is 54°C. This method of purification for compound VII is successful only when the material is heated rapidly to the required distillation temperature.

If compound VII in pure form is heated slowly to 130°-160°C under a reduced pressure of 0.1 mm Hg, it decomposes in the following manner:

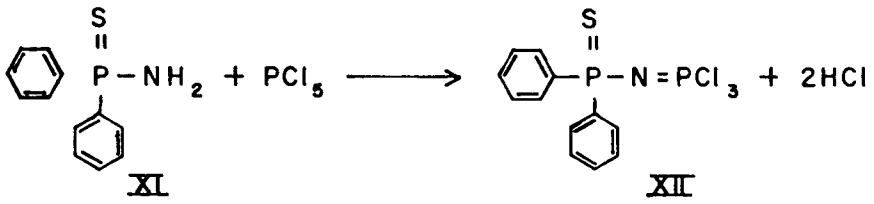
$$n\,O{=}\overset{\displaystyle C_6H_5\ \ C_6H_5}{\overset{|}{P}{-}N{=}\underset{|}{P}}{-}Cl \rightarrow n\,O{=}\overset{\displaystyle Cl}{\overset{|}{P}}{-}C_6H_5 + \left[NP(Cl)C_6H_5\right]_n$$

VII VIII IX

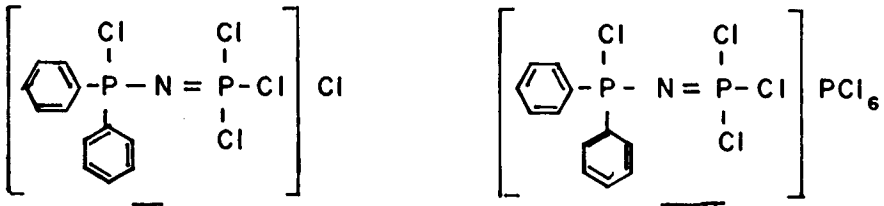
Compound VIII is volatile and can be distilled off. Compound IX is polymeric; it is resinous and soluble in organic solvents such as benzene, and so forth.

We then attempt to prepare the isomeric form of compound I, that is, compound X. The following appeared to be a suitable procedure:

Compound XI was first reacted with PCl_5; this occurs primarily in the sense of a Kirsanov reaction, that is, the two hydrogen atoms attached to the nitrogen are substituted by a PCl_3-group. This leads to compound XII. Further action of PCl_5 causes removal of the sulfur in compound XII with replacement by chlorine. Thus, depending on the amount of PCl_5 used, either compound X itself or its hexachlorophosphate derivative (XIII) is formed.



XI XII



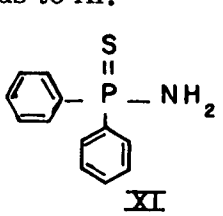
X XIII

The preparation of the starting materials $(C_6H_5)_2P(S)Cl$ and $(C_6H_5)_2P(S)NH_2$ from this compound has already been described in principle (Reference 1).

Contrary to the procedure for the corresponding dimethyl compound, $(C_6H_5)_2P(S)Cl$ can be synthesized from $(C_6H_5)_2PCl$ and S without the presence of a catalyst when the stoichiometric mixture is heated at 160°-170°C until the odor of phosphine is no longer noticeable (even after cooling).

$(C_6H_5)_2P(S)Cl$: n_D^{20} =1.6628; b p $_{0.2}$: 155-159°C.

Reaction of this compound with NH_3 leads to XI.



XI

C. PREPARATION OF $[(C_6H_5)_2P(Cl)=N-PCl_3]PCl_6$ (XIII)

A solution of 14.4 g (0.062 mole) of $(C_6H_5)_2P(S)NH_2$ in 200 ml of dry chloroform is placed in a flask provided with a stirrer and a reflux condenser fitted with a drying tube. Forty grams (0.19 mole) of PCl_5 are added with stirring and the mixture is heated slowly to 50-60°C. After the vigorous evolution of HCl has subsided (1/2-1 hour), the mixture is boiled under reflux for another 2 hours. Most of the solvent is then distilled off, and the cooled oily residue is treated with dry benzene. This first benzene extract is poured off and the residue is shaken again twice with fresh portions of benzene. After the third wash, the reaction product separates in pale greenish-yellow crystals. The yield of the already very pure crude product is 90-100 percent; the substance can be recrystallized from small amounts of chloroform (100 ml).

Analysis of XIII: $C_{12}H_{10}Cl_{10}NP_3$ (615.72)

Required C 23.41%, H 1.64%, Cl 57.58%, N 2.28%, P 15.09%

Found: C 24.65%, H 2.18%, Cl 57.5%, N 2.28%, P 14.6%

This substance is very hygroscopic and can be handled only in an absolutely dry atmosphere. It is difficultly soluble in non-polar solvents such as benzene, carbon tetrachloride, and petroleum ether and soluble in tetrachloroethane, chloroform, and phosphorus oxychloride. Compound XIII melts at 163°-166°C. The molecular weight measured in nitrobenzene is 285 (calc. 615.72), since the salt dissociates in this solvent. The assumption that dissociation into two univalent ions occurs was confirmed by measurement of the equivalent conductivity in nitrobenzene.

$(\lambda = 0.5.10^{-7}\,\Omega^{-1}cm^{-1})$.

$\Lambda_c(20°C) = 21\,\Omega^{-1}, cm^{-1}, mole^{-1}$ $(c = 0.8 \cdot 10^{-2}$ mole/e).

D. PREPARATION OF $[(C_6H_5)_2P(Cl)=N-PCl_3]Cl$ (X)

The chloride X is obtained in the same way as XIII when a mole ratio of $(C_6H_5)_2P(S)NH_2$: PCl_5 of 1:2 is employed. After washing with benzene X remains as an oil. The product crystallizes when the remaining traces of solvent are pumped off in vacuo.

A compound containing oxygen which is isomeric with VII can be prepared by the action of SO_2 on X and XIII. This compound (XIV) is obtained in the following way: Dry SO_2 is passed into $[(C_6H_5)_2P(Cl)=N-PCl_3]PCl_6$ in a flask fitted with a gas inlet and a gas outlet tube. The crystalline mass liquefies; after the mixture has become homogeneous, SO_2 is then passed in for another hour. SO_2, $SOCl_2$ and $OPCl_3$ are then removed in an aspirator vacuum. The residue is distilled rapidly in vacuo at 205°-215°C/0.01 mm Hg, care being taken to select a short distillation path. Yield: 90 % of theory.

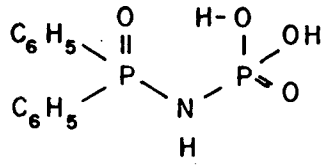
Analysis of XIV: $C_{12}H_{10}Cl_3NOP_2$ (352.54)

Required: C 40.88%, H. 2.86%, Cl 30.17%, N 3.97%, C 4.54%, P 17.57%

Found: C 40.81%, H 2.91%, Cl 30.22%, N 3.98%, O - P 17.92%

The cryoscopically determined molecular weight in benzene was 368 (calc. 352.5). The compound is a pale yellow, oily liquid. It is considerably less sensitive towards hydrolysis than the salt is, and is soluble in benzene, dioxane, and carbon tetrachloride.

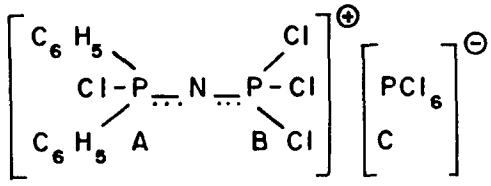
Careful hydrolysis of XIV leads to compound XV, a colorless crystalline substance (mp 201°-203°C). It is possible that the high melting point of compound XV is due to hydrogen bonding.



XV

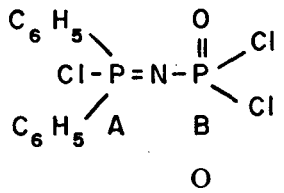
The structures of compounds XIII and XIV were established from their nuclear magnetic resonance spectra. The chemical shifts arising from the P^{31} nuclei were measured with a VARIAN resonance spectrometer, using a radio frequency of 24.3 megacycles and a magnetic field strength of ca. 14 K Gauss.

Measurements made on a solution of compound XIII dissolved in $OPCl_3$ gave the following results for the chemical shifts: A = $-42.3 \cdot 10^{-6}$, B = $-14.3 \cdot 10^{-6}$, and C = $+305 \cdot 10^{-6}$, compared with 85 % orthophosphoric acid as standard. From this it is evident that the compound contains three non-equivalent phosphorus nuclei. The resonance signals can be accounted for by the following structure:



XIII

It would be expected that spin-spin coupling between nuclei A and B should give rise to splitting of the resonance maxima A and B. However, this was not found; the intensity of the resonance signals was too weak, owing to the limited solubility of the substance. The compound formed from the reaction of SO_2 with X is more suitable for n. m. r. studies, since it can be examined directly in liquid form. The spectrum obtained is shown in Figure 1; it is apparent from this that the reaction product is a uniform substance. The form of the spectrum is typical for a compound which contains two nonequivalent phosphorus nuclei connected by a nitrogen atom. The observed chemical shifts A = $-29.05 \cdot 10^{-6}$ and B = $+8.8 \cdot 10^{-6}$ (with respect to 85 percent orthophosphoric acid) show that both P-nuclei belong to phosphorus with the coordination number four. The positions of A and B would suggest the arrangement



XIV

since in other compounds containing the $N-PCl_2$ group a chemical shift δ of the same order of magnitude was found as for B. Band A originates from the much less strongly shielded phosphorus nucleus A. From the extent of splitting in the two doublets, the surprisingly large coupling constant of $J = 63.1 \pm 2.5$ c.p.s. is obtained for the spin-spin coupling. When the spectrum is analyzed according to the method of Pople, Schneider, and Bernstein, the value 0.071 is found for $J/\nu_o \delta$, the magnitude of which is decisive for the form of the spectrum. A theoretical spectrum is thus obtained such as has already been described at an earlier date for the compound $Cl_3P=N-P(O)Cl_2$. The observed spectrum and the computed one are in good agreement.

It is remarkable in the reaction of XIII with SO_2 that only XIV is formed and not also compound XVI; SO_2 apparently always attacks first at the P atom which is most strongly electronically shielded.

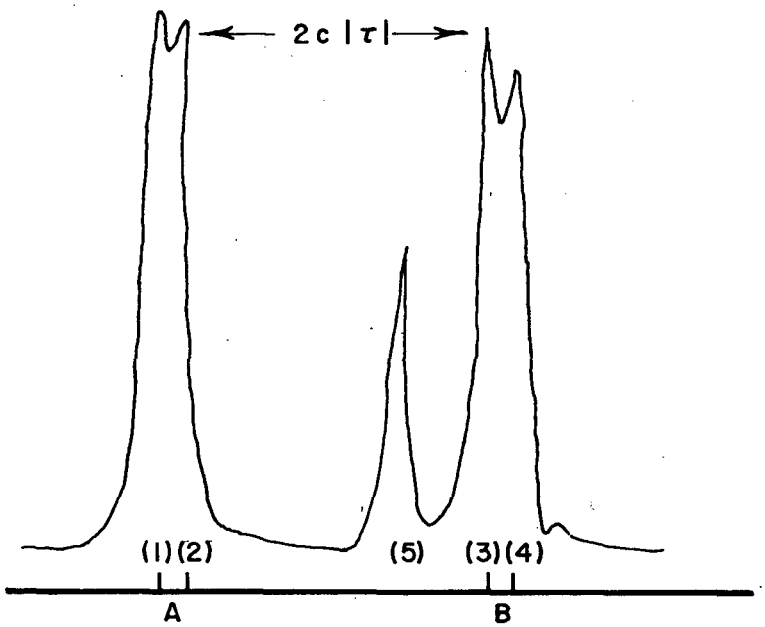
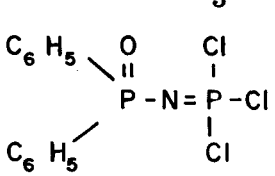
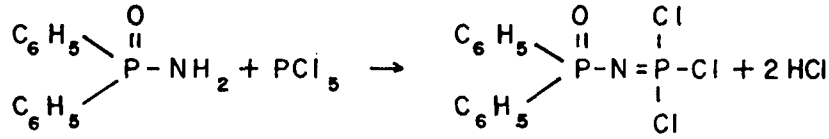


Figure 1. P^{31} Resonance Spectrum of Compound XIV. $\delta(1) -30.3 \cdot 10^{-6}$, $\delta(2) -27.8 \cdot 10^{-6}$, $\delta(3) +7.3 \cdot 10^{-6}$, $\delta(4) +10.0 \cdot 10^{-6}$, $\delta(5)(OPCl_3) -2.2 \cdot 10^{-6}$.



XVI

The attempt was made to prepare XVI by another route, namely, according to the following equation:



XVII XVI

However, it was found that XVII does not react in this way in the sense of a Kirsanov reaction; instead, a relatively large amount of $OPCl_3$ and $(C_6H_5)_2P(O)Cl$ is formed together with a series of phosphorus nitride compounds.

For further details concerning these experiments, please refer to Scientific Report No. 1 (Contract AF 61(052)-682) (Reference 2).

SECTION III

ATTEMPTS TO PREPARE POLYMERS FROM PHOSPHORUS NITRIDE SALTS CONTAINING PHENYL GROUPS

It was already mentioned that product VII, which contains oxygen, can be produced fairly easily from I. In pure form, VII is crystalline and melts at 54°C.

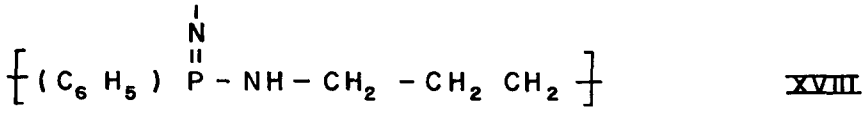
It was also stated that when compound VII is heated slowly to 130°-180°C under reduced pressure, decomposition occurs and compound VIII is formed together with the polymer IX.

The following should be noted with respect to the thermal decomposition of VII: Normally, when VII is slowly heated to 150°C it decomposes to form VIII and IX, but in certain instances decomposition does not occur even when the substance is heated for several days at 150°-180°C. In this event, VII can be distilled as a bright yellow oil at 210°-213°C/0.01 mm Hg; the distillate solidifies at 54°C. Samples of VII which have been purified in this way can be redistilled when they are heated rapidly to 210°C in vacuo. However, when compound VII in pure form is heated very slowly and the temperature is maintained at 150°-180°C for a longer period of time, decomposition into VIII and IX takes place. An explanation could not be found for the fact that VII can occasionally be distilled without decomposition and that at times the thermal decomposition into VIII and IX can only be realized with difficulty. The behavior of compound VII was not altered when compound I or $OSCl_2$ was added to it.

The following is to be reported in connection with further reactions of IX with diamines: When the reaction with hexamethylenediamine was carried out in boiling benzene, a colorless precipitate was formed. The mean empirical formula for this material was found to be

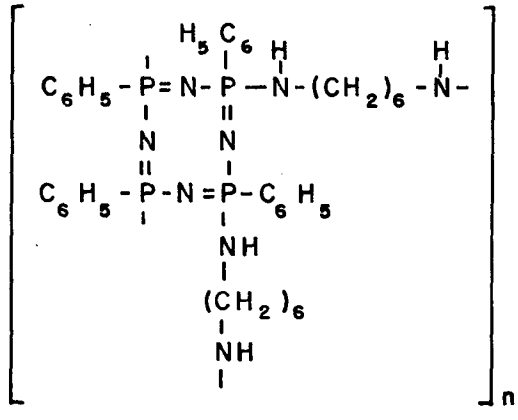
$$A = \left[PN_{2.1}\ C_{9.4}\ H_{13.9}\ O_{0.3} \right],$$

which shows that the product is polymeric. According to the analysis, the polymer appears to contain groups of type XVIII.



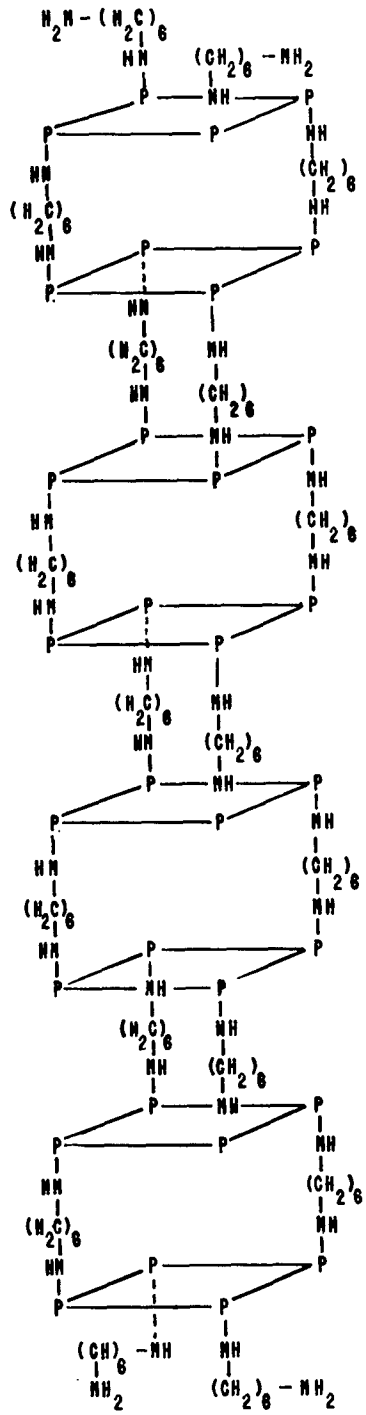
XVIII

Both the elementary analysis and the determination of the terminal groups by acidimetric titration showed that one free amine group is contained for every eight groups of type XVIII. From this it can be inferred that probably XIX and not XVIII is the true structural component.



XIX

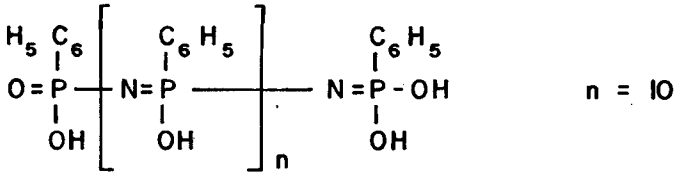
Thus, the polymer is a derivative of tetrameric phosphorus nitrilic chloride. The determination of the terminal groups shows that three of these tetramers are connected by hexamethylenediamine bridges. Chain cleavage then occurs and four terminal phosphorus atoms are substituted by hexamethylenediamine groups in such a way that four free amino groups remain. The structure of the polymer is represented by the sketch given for furmula XX.



XX

In this sketch, the nitrogen atoms which connect the phosphorus atoms in the phosphorus nitrilic tetramers and the phenyl group attached to each P atom have been omitted. It is to be noted that the phosphorus nitrilic ring systems are not planar, but of undulating form.

Polymer XX is insoluble in water; when boiled in water for two hours it loses 1.4 percent of its original weight, although the same treatment with 2n caustic soda leads to a loss in weight of only 0.5 percent. After two hours of boiling in 2n hydrochloric acid, on the other hand, 63.2 percent reduction in weight is observed. This simple experiment is sufficient to show that compound XX is hydrolyzed easily only in acidic medium. The hydrolysis leads to the formation of hexamethylenediamine (insoluble in water), soluble phenylphosphonic acid, $C_6H_5P(O)(OH)_2$, and polymeric phenylphosphonic acid (formula XXI):



XXI

The yield of the latter is about 48 percent; it is difficulty soluble in water, remains undissolved when boiled with hydrochloric acid and has an unsharp melting point at about 190°C. Compound XXI has a characteristic infrared spectrum.

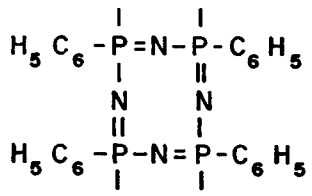
Compound XX shows the following thermal behavior: when heated in air it changes color at 230°C. At this temperature an exothermic reaction sets in, as can be determined by detailed analysis of the corresponding heating curves, but the thermal balance does not indicate a change in weight of the substance. Loss in weight is first observed at 350°C, and amounts finally to 39.4-43.2 percent. The thermal degradation which then sets in is fairly complex. First amine is split off and then, at higher temperature, the phenyl residue. Finally, OPN is formed, which volatilizes above 670°C.

When XX is heated to 280°C under nitrogen in a tube, the material can be pressed into a firm tablet which has the same analytical composition as the original substance XX. The tablet is stable at 280°C; it becomes darker in color when heated to this temperature in air, but does not change in appearance when heated in nitrogen.

If IX is reacted with octamethylenediamine instead of with hexamethylenediamine, a polymeric substance with the empirical formula

$$B = PN_{2.2}\ C_{10.8}\ H_{16.9}\ O_{0.2}$$

is obtained. The formula of this polymer was determined in the same way as for the reaction product with hexamethylenediamine. Here too, the polymeric structure can be derived from the tetrameric phosphorus nitrilic system XXII.



XXII

In this case, determination of the terminal groups showed that ten tetraphosphorus nitrilic systems are interconnected and that four terminal phosphorus atoms each bear one free octamethylene amino group.

This substance B is also fairly resistant towards hydrolysis. The loss in weight following a two hour period of boiling was found to be as follows: with water, 1.6 percent, with 2n caustic, 0.6 percent, and with 2n HCl 77.4 percent. Again, acidic hydrolysis leads to polymeric phenylphosphonic acid (XXI) in about 50 percent yield together with ordinary phenylphosphonic acid and octamethylenediamine. This polymer B produced from IX and $H_2N(CH_2)_8NH_2$ first undergoes loss in weight at between 320°C and 350°C when it is heated in air. The first stage of the thermal decomposition is complete at 450°C. The substance thus obtained is dark in color and has the empirical formula

$$C = NP_{1.8}\ C_{5.5}\ H_{10.0}\ O_{9.0}$$

If the polymer B obtained from octamethylenediamine is heated to 280°C in a glass tube closed at one end, the substance can likewise be pressed into a firm tablet whose composition is the same as that of the original material. The tablet can be heated to 280°-285°C without change. The presence of air causes a slight superficial darkening of color which does not occur under a blanket of nitrogen.

Analogous experiments were conducted using p-phenylenediamine and IX as starting materials. The former was dissolved in xylol and the latter in benzene. The mixed solvents and their dissolved components were heated under reflux for two hours. The substance obtained was found to have the empirical formula

$$D = PN_{2.2}\ C_{10.0}\ H_{10.1}\ O_{0.2}\ ,$$

according to the same method described. It could be shown that the number of chain members connected by p-phenylenediamine is smaller than that in the case of aliphatic diamines. It was found that four free amino groups are present for every three tetrameric phosphorus nitrilic systems (XXII).

The behavior of this polymer D towards hydrolysis was in complete accord with that of the other polymers described. Heating with water for two hours led to a reduction in weight of 3.3 percent. Substance XXI was again formed in the acidic hydrolysis. A fairly hard, black material was obtained when the product was pressed at 280°C. Formula:

$$PN_{2.0}\ C_{9.7}\ H_{9.5}\ O_{0.3}$$

No loss in weight was observed up to 385°C. A polymer was also formed when compound IX was treated with m-phenylenediamine in benzene; the empirical formula is represented by

$$E = PN_{2.7}\ C_{11.1}\ H_{11.2}\ O_{0.3}$$

This substance E was found to contain more NH_2 groups than in the case of the other polymers. Here, there are eight amino groups for every three tetrameric phosphorus nitrilic systems. This indicates that the linking is different from that of the other polymers, in which fewer end-groups are present. The hydrolytic behavior is in agreement with this; after two hours of boiling with water 10.8 percent loss in weight occurred, and under the same conditions with 2n HCl 82.7 percent reduction in weight together with the formation of XXI was observed.

When the polymer E is heated under nitrogen, loss in weight sets in already at 180°C and amounts to 15.5 percent at 330°C. The substance then obtained is stable up to about 490°C. Under the action of heat, the polymer splits off diamine:

$$P_3 N_8 C_{33} H_{33} O \rightarrow N_2 C_6 H_8 + P_3 N_6 C_{27} H_{25} O.$$

Hence a further condensation reaction takes place between 180°C and 330°C.

When the polymer E formed from IX and m-phenylenediamine is heated in a closed glass tube at 260-270°C and the material is pressed, a viscous, brown melt is obtained and not a tablet. This is understandable when we assume that the structure of this polymer E is less symmetrical than those of the other polymers.

Attempts to prepare a polymer from IX and 2,6-dichlor-p-phenylenediamine were unsuccessful.

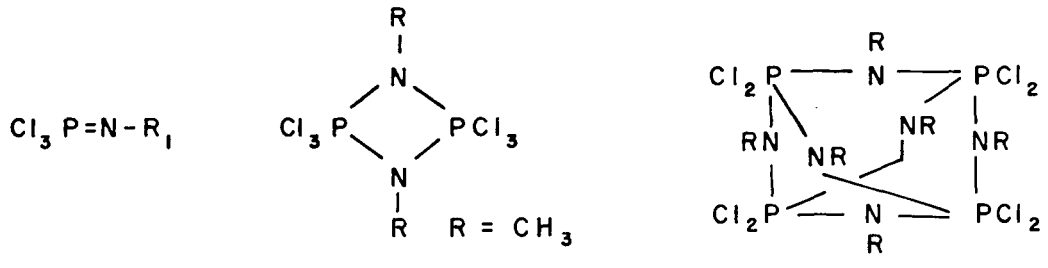
It can be concluded that IX reacts with diamines to form polymers which can be thermoplastically shaped and which are stable up to about 300°C. These substances hydrolyze in acidic medium. The materials obtained by us have molecular weights of about 1400, 6000, and 8000. The highest molecular weight was obtained with octamethylene diamine as reagent.

SECTION IV

THE PREPARATION OF NEW PHOSPHORUS NITRIDE DICHLORIDES WHICH MAY BE SUITABLE FOR THE PRODUCTION OF POLYMERIC PHOSPHORUS-NITROGEN COMPOUNDS

The experiments in this connection were surprisingly successful, and a new type of phosphorus nitride dichloride was isolated. It is already generally known that the reaction of PCl_5 with amines leads to compounds of either Type XXIII or Type XXIV. According to Kirsanov, the basicity of the amine is a determining factor as to whether a monomer (XXIII) or a four-membered ring system (XXIV) is formed. Our studies concerned the reaction of PCl_5 with methylamine and with methylammonium chloride $\left[CH_3NH_3 \right] Cl$. We found that the four-membered ring system XXIV ($R = CH_3$) is obtained in excellent yield when completely dry methylammonium chloride is heated with PCl_5 in tetrachloroethane for eight hours at 145°C. However, if the ammonium salt contains moisture (several percent), a brown oil from which crystals slowly separate is formed together with the crystalline material XXIV. After recrystallization from benzene, the substance obtained from the oil had a composition corresponding to $P_2N_3C_3H_9Cl_4$. Its molecular weight was determined ebullioscopically in dichloroethane; the results indicated that the formula is expressed by $P_4 \left[N(CH_3) \right]_6 Cl_3$. Further information relating to the structure of this compound was provided by measurement of the nuclear magnetic resonance spectrum of the P^{31} nuclei. The spectrum was plotted in solution in benzene. Only one resonance maximum with a chemical shift of +74.3 appeared. This shows that the P-atoms are chemically equivalent and that phosphorus is pentavalent in this compound. If comparison is made with the n.m.r. spectrum of compound XXIV, it is seen that both chemical shifts are of the same order of magnitude. The P^{31} resonance spectrum of compound XXIV indicates a chemical shift of +78.2 (referred to 85 percent phosphoric acid). It can be concluded on the basis of this evidence that the new compound must possess a cage structure (XXV). In this type of cage, the phosphorus atom is surrounded by five ligands; these ligands form a tetragonal pyramid.

In a closed tube, compound XXV is stable up to about 400°C, whereupon it then decomposes without melting. The relatively high thermal stability of XXV would appear to make further reactions with this compound very promising. We are investigating the reaction with SO_2, and it would seem that all the Cl atoms in compound XXV can be replaced by four oxygen atoms. In compound XXIV, four Cl atoms are replaceable by two oxygen atoms. Together with such additional reactions, we are of course attempting to find ways of improving the yield of XXV in its synthesis from PCl_5 and methylammonium chloride.



XXIII XXIV XXV

SECTION V

ATTEMPTS TO OBTAIN POLYMERS FROM TRIMERIC PHOSPHORUS NITRIDE CHLORIDE, IN WHICH THE SIX-MEMBERED RING SYSTEMS OF THE PHOSPHORUS NITRIDE DICHLORIDE ARE INTERCONNECTED BY N-SO_2-N BRIDGES

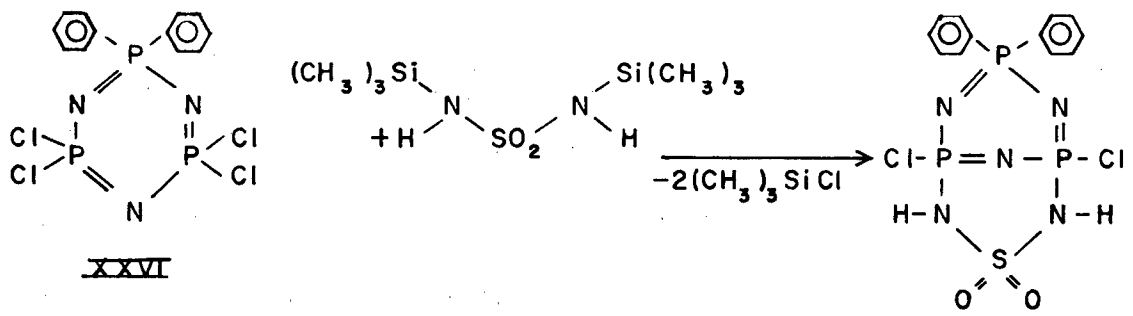
A discussion of the experiments follows:

First, the starting material for the subsequent reaction was prepared from tris phosphorus nitride dichloride by a Friedel-Crafts reaction. Two chlorine atoms of tris phosphorus nitride dichloride can be substituted in good yield in boiling benzene with the help of finely ground, anhydrous aluminum chloride. Hydrolytic fission of the diphenyl derivative thus formed leads to diphenyl phosphonic acid, $(C_6H_5)_2POOH$, in quantitative yield. This provides direct proof of the fact that both phenyl groups are attached to the same phosphorus atom.

This phenylation by the Friedel-Crafts method is specific for the substitution of two chlorine atoms, regardless of the amount of aluminum chloride used. The reaction proceeds first by way of the addition compound $P_3N_3Cl_6 \cdot 2AlCl_3$, a pale yellow substance which can be isolated, to a red ternary complex $\left[P_3N_3Cl_4 \cdot (C_6H_6)_2 \right]\left[AlCl_4 \right]_2$ and then finally to the desired product.

Diphenyl-tetrachloro-tris-phosphorus nitride (XXVI) crystallizes in colorless leaflets which melt at 97°C. This compound is not quite as stable as trisphosphorus nitride dichloride, and cannot be distilled without decomposition. However, it can be purified by recrystallization from low-boiling petroleum ether. Di- and tetrasubstituted derivatives can be obtained by reaction with aniline or ammonia.

The next aim in mind was to react this starting material in such a way as to replace the chlorine atoms of the cyclic, quasi-aromatic system by basic groups and if possible substitute two non-proximate chlorine atoms simultaneously by a diamide grouping, thus leading to exocyclic systems involving the original six-membered ring. This is illustrated by the following equation:



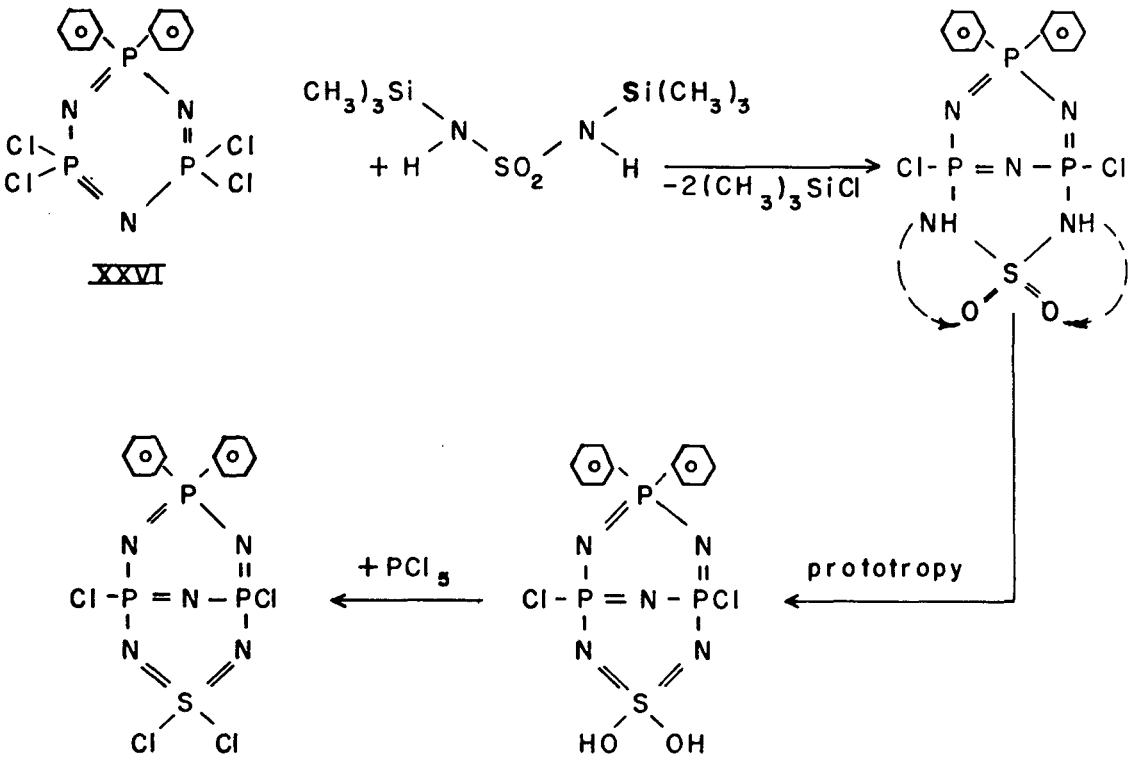
XXVI

It was hoped that by blocking one of the phosphorus atoms in the ring, polymerization of the reaction product could be retarded and extensive crosslinking hindered.

In the following reactions, the diphenylated reagent was employed in molar excess in order to drive the reaction as far as possible towards the formation of the desired product.

A. THE REACTION OF DIPHENYLTETRACHLORO-TRIS-PHOSPHORUS NITRIDE WITH N,N'-BISTRIMETHYLSILYL SULFAMIDE

For steric reasons, the following course of reaction was expected, whereby some degree of polymerization resulting from intermolecular cross-linking was not unlikely:



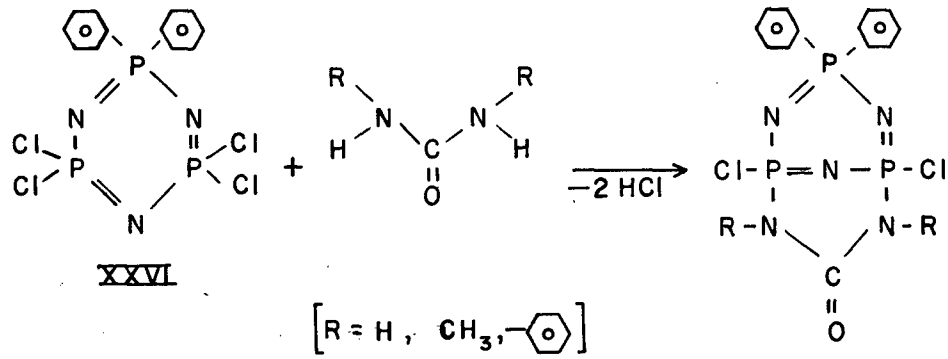
The possibility of prototropy then had to be taken into account; this would enable chlorination of the OH-groups thus formed in a structure consisting of two condensed six-membered rings.

The reaction was first carried out in absolute ether (in which both reagents are soluble) by boiling under reflux for four hours. The solution was then partially evaporated and allowed to cool, whereupon unaltered diphenyltetrachloro-tris-phosphorus nitride precipitated out in pure form (m p 97°C; the IR spectrum was identical with that of the initial reagent). The unchanged bistrimethylsilyl sulfamide remained in solution.

Even the action of higher temperatures by means of higher-boiling solvents, for example, benzene, 1,2-dichloroethane, and symmetrical tetrachloroethane together with the application of the Ruggli-Ziegler dilution principle did not lead to the desired compound. In spite of wide variation in reaction time (from one to forty hours), no chemical change occurred. Even when unsubstituted sulfamide was introduced, no reaction took place, as could be shown by complete recovery of the starting materials (identification by melting point and comparison of the IR spectra).

B. THE REACTION OF DIPHENYLTETRACHLORO-TRIS-PHOSPHORUS NITRIDE IN TURN WITH DIMETHYLUREA, DIPHENYLUREA, AND UREA IN SOLUTION

In this case, it was considered feasible that replacement of the chlorine atoms by NH- or NR-groups could occur, whereby in this instance the CO-group instead of the SO_2-group would be built into the expected bicyclic system. Here too, allowance was to be made for at least some degree of cross-linking of the molecules. 1, 2-Dichloroethane was employed as a solvent; this dissolves dimethylurea when hot. No chemical change was observed after several hours of boiling under reflux; this fact was substantiated by the recovery of the starting materials. The same applied for a reaction in boiling benzene lasting three days.



XXVI

[R = H, CH_3, –⬡]

Similarly, no reaction was observed to occur when N, N'-diphenylurea or unsubstituted urea were introduced in place of N, N'-dimethylurea. In all these experiments we attempted to induce a reaction by increasing the polarity of the solvent, for example, with mixtures such as benzene/nitrobenzene 1:1 and symmetrical tetrachloroethane/phosphoryl chloride 1:3, but without success.

C. THE REACTION OF DIPHENYLTETRACHLORO-TRIS-PHOSPHORUS NITRIDE WITHOUT A SOLVENT

Under these conditions, the diphenyl derivative was mixed and fused with each of the reagents listed above without the presence of a solvent. The mixture was stirred vigorously and nitrogen was passed in. Subsequent processing of the ground product showed in every case that either only the starting materials were recoverable or that, depending on the reaction temperature, partial or complete decomposition had set in. The latter case was manifested in the charring and evolution of HCl which became evident at temperatures above 120°C.

D. THE REACTION OF TRIS-PHOSPHORUS NITRIDE DICHLORIDES WITH INORGANIC DIAMIDES AND THEIR DERIVATIVES

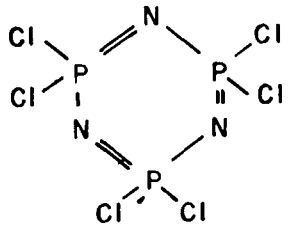
1. The reaction of tris-phosphorus nitride dichloride with dimethylurea, urea, sulfamide, and N,N' -bistrimethylsilyl sulfamide

The reason for carrying out analogous reactions with the unsubstituted $N_3P_3Cl_3$-ring (XXVII) in view of the lack of success with the diphenyl derivative was that in this instance the six chlorine atoms are known to be somewhat more easily replaceable than those in the diphenyl compound, where the four chlorine atoms are deactivated by the introduction of the two phenyl groups, thus impeding ease of substitution (Reference 3). The desired reactions would be expected to proceed with greater ease in the case of the hexachloro compound, admittedly with the disadvantage that the tendency towards polymerization would probably be greater.

The reactions were conducted for the most part in boiling benzene with successively increased reaction times (from two hours to two days). However, the basicity of the reagents used appeared to be insufficient to cause nucleophilic substitution of the chlorine atoms. Melting point determinations and infrared spectra showed that no chemical change had occurred.

2. The reaction of tris-phosphorus nitride dichloride (XXVII) with N, N' -Dimethylurea in the presence of strong bases

The addition of a strong Lewis base such as pyridine or triethylamine, which would immediately take up any HCl formed, could conceivably cause an appreciable shift in the thermodynamic equilibrium in the direction of formation of the stable hydrochloride of the base and hence also in the direction leading to the desired product.



XXVII

After the reaction components had been boiled in benzene for two days, a syrupy mass was formed; when allowed to cool, this product solidified to a glass whose composition corresponded neither to that of the desired compound nor to a polymer of the latter. This material seemed to consist largely of hydrochloride derivative of the base. Attempts to separate this hydrochloride from the accompanying product by extraction methods were unsuccessful; no definite compound could be isolated although numerous solvents such as ether, chloroform, carbon tetrachloride, benzene, 1, 2-dichloroethane, and water were applied.

E. REACTION OF $N_3P_3Cl_6$ and of $(C_6H_5)_2N_3P_3Cl_4$ WITH IMIDODISULFAMIDE

No reaction occurred in benzene and in 1,2-dichloroethane; the starting materials were recovered and identified by their infrared spectra.

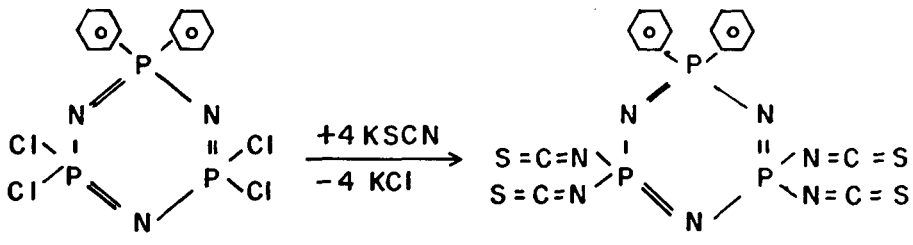
It is apparent that in all such attempts to induce substitution in the quasiaromatic P-N-ring system, the basicity of the reagents employed was too weak to cause replacement of the relatively firmly attached chlorine atoms in this ring, which is mesomerically stabilized. Whereas the application of the bases NH_3, NH_2CH_3, and $HN(CH_3)_2$ led to well-defined, crystalline substitution products, no chemical reaction was observed when the above-mentioned, relatively weak bases were employed, even when the mole ratios, temperature, and reaction times were widely varied. The subsequent addition of strong bases as HCl-acceptors also did not lead to the formation of definite compounds. It would seem that when more drastic conditions are chosen, decomposition rather than a unique reaction occurs.

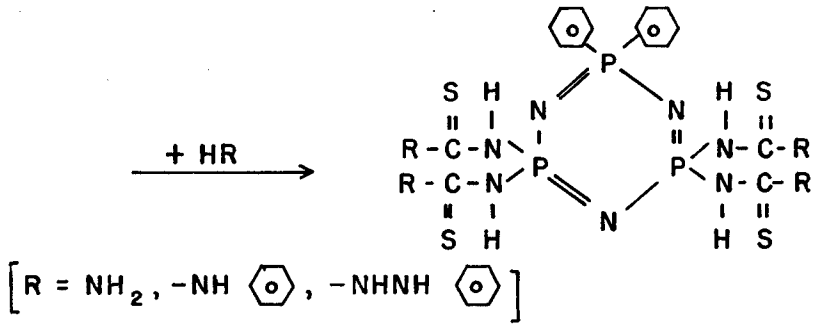
F. SUBSTITUTION OF CHLORINE ATOMS IN THE QUASIAROMATIC RING SYSTEM BY MEANS OF THE PSEUDOHALIDE GROUPS - SCN AND - OCN

1. The reaction of diphenyltetrachloro-tris-phosphorus nitride with potassium thiocyanate

In 1959, Otto and Audrieth (Reference 4) reported the preparation of the persubstituted compounds $\left[NP(SCN)_2 \right]_3$ and $\left[NP(SCN)_2 \right]_4$, which they obtained from the action of potassium thiocyanate on the corresponding chlorides, using absolute acetone as solvent.

I now attempted to synthetize the compound $(C_6H_5)_2N_3P_3(SCN)_4$ along similar lines. This product would presumably open the way to numerous reaction possibilities with the formation of many new compounds. The following reaction seemed feasible:





The reaction was carried out in dried acetone; potassium thiocyanate is fairly soluble in this solvent, and the diphenyltetrachloro-tris-phosphorus nitride, also dissolved in acetone, was dropped into the boiling KOCN solution. Boiling was continued under reflux for several hours. The white precipitate which was soon formed was filtered off at the end of the reaction time. The chlorine analysis and the IR spectrum showed that this material was potassium chloride. With a reaction time of twelve hours and a threefold excess of potassium thiocyanate, a quantity of potassium chloride corresponding to about 90 percent conversion was obtained. The KCl was separated and the acetone filtrate cooled to -80°C. However, no solid crystallized out, whereupon the dissolved excess of potassium thiocyanate had to be removed by precipitation with benzene. The yellow solution which remained was evaporated. The yellow residue thus obtained had a melting point higher than 220°C and was soluble only in acetone and in benzene. The IR and n.m.r. spectra showed that the material was not a unique, pure substance. Attempts to isolate a pure compound by extraction were not successful, although n-octane, petroleum ether, ether, tetrachloroethane, and chloroform were used for this purpose.

The infrared spectrum clearly showed the presence of an -NCS-group at $\tilde{\gamma}$ = 1950-2050 cm^{-1} and the n.m.r. spectrum revealed two peaks. However, comparsion with the position of the $-P(NCS)_2$ group in $N_3P_3(SCN)_6$ did not offer definite proof of the existence of the hypothetical compound $(C_6H_5)_2N_3P_3(SCN)_4$. The analysis of the reaction product was also disappointing in this respect:

Calculated for $(C_6H_5)_2N_3P_3(SCN)_4 = C_{16}H_{10}P_3N_7S_4$ (Microanalysis No. 25084).

Required: C 36.87%, H 1.92%, P 17.82%, N 18.82%, S 24.57%

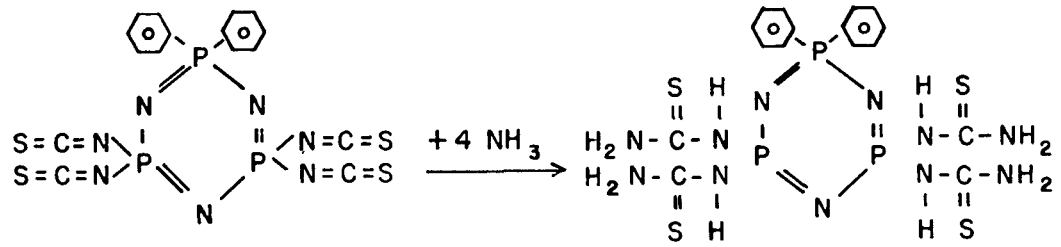
Found: C37.6%, H 3.27%, P 19.0%, N 14.6%, S 15.2% Cl 8.5%

On the basis of the results of analysis and the n.m.r. spectrum, it is, however, not improbable that the expected compound was present, but impurified by residual starting material; this is substantiated by the value found in the analysis for chlorine and by the presence of two bands in the n.m.r. spectrum. Nevertheless, separation of this mixture by physical means such as extraction or reprecipitation has not yet proved successful.

I now attempted to achieve isolation by chemical means, that is, by further reaction, in the hope that the new products formed could be separated more easily.

G. THE REACTION OF DIPHENYLTETRATHIOCYANATO-TRIS-PHOSPHORUS NITRIDE WITH GASEOUS AMMONIA

According to Otto and Audrieth (Reference 4), this reaction should lead to an addition of the ammonia molecule to the NCS-group attached to the six-membered ring, as illustrated by the following equation:



The thiourea group formed in this way should then be identifiable by its characteristic infrared absorption.

A solution in benzene of the crude product presumably containing $(C_6H_5)_2N_3P_3(SCN)_4$ was boiled under reflux for three hours and dried ammonia sparged in during this time. The analysis of the yellow-brown substance then obtained showed values which were not compatible with any of the conceivable courses of reaction.

Found: C 40.80 %, H 5.32 %, N 19.6 %, P 18.2 %, S 10.6 %
(Microanalysis No. 25437)

H. THE REACTION OF DIPHENYLTETRATHIOCYANATO-TRIS-PHOSPHORUS NITRIDE WITH LIQUID AMMONIA

In order to ensure complete amidation, the same reaction was repeated, this time in liquid ammonia. For this purpose, a NIEDENZU apparatus was employed. The crude starting product was soluble in liquid NH_3; after the latter was allowed to evaporate, a yellow substance was obtained which had the following analysis:

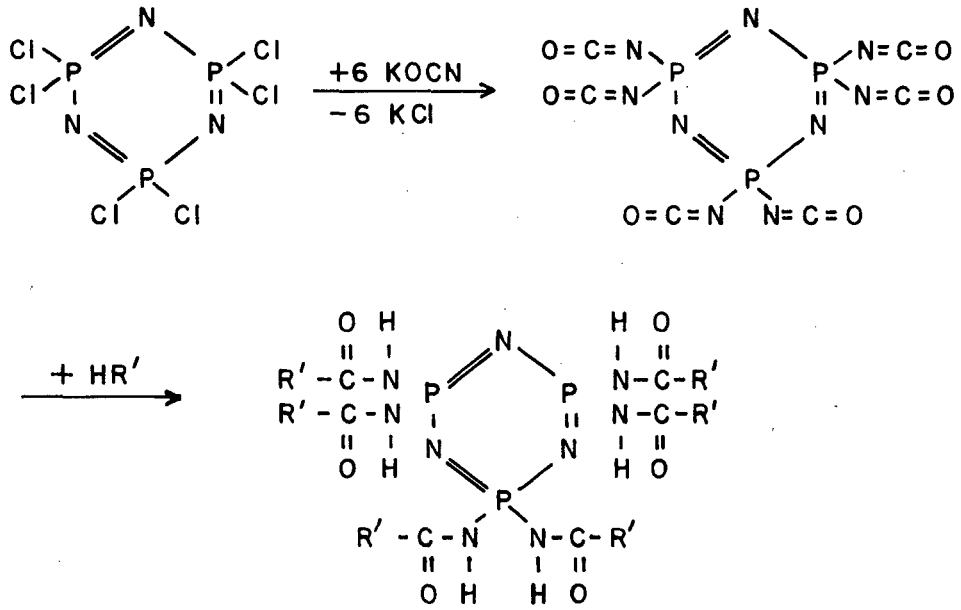
C 35.12 %, H 5.09 %, N 20.9 %, P 14.4 %, S 14.0 %, Cl 8.0 %
(Microanalysis No. 25600)

Here again, the values for sulfur and nitrogen are far too low. The IR spectrum indicated that unchanged NCS-groups were still present. The analyses showed repeatedly that the atomic ratio S:P was only 3:3, which is not in agreement with that of the expected compound.

I. REACTIONS OF THE COMPOUNDS $N_3P_3Cl_6$ and $(C_6H_5)_2N_3P_3Cl_4$ WITH POTASSIUM CYANATE AND WITH SILVER ISOCYANATE

I now attempted to replace the chlorine atoms in the ring system by NCO-groups; this reaction has not as yet been reported in the literature. Cyanate derivatives formed in this way should then be able to react further with proton-active compounds in a manner similar to that for thiocyanate derivatives.

As in the case of potassium thiocyanate, the reactions of $N_3P_3Cl_6$ and of its diphenyl derivative with potassium cyanate were carried out in acetone. Repeated experiments consistently led to the result that the starting materials could be quantitatively recovered (comparison of infrared spectra and melting points).



The reactions with AgNCO in benzene and in symmetrical tetrachloroethane also did not lead to the desired compound. No silver chloride as reaction product could be detected.

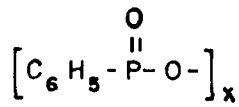
SECTION VI

ADDITIONAL ATTEMPTS TO PREPARE POLYMERIC PHOSPHORUS–NITROGEN COMPOUNDS

It seemed feasible that useful polymers could also be prepared by connecting phosphorus atoms with coordination number four by way of oxygen atoms instead of nitrogen atoms.

In order to achieve this, we reacted phenylchlorophosphine with dimethyl sulfoxide. When we reacted $C_6H_5PCl_2$ with dimethyl sulfoxide $(CH_3)_2SO$ in a mole ratio of 1:1, we obtained monomeric C_6H_5-P(O)Cl_2. We employed tetrachloroethane as solvent and a reaction temperature of 70-80°C. The yield of C_6H_5-P(O)Cl_2 was 30 percent of theory. CH_3-S-CH_2Cl was formed as by-product. Hydrolysis of C_6H_5-P(O)Cl_2 with water gave the phosphonic acid C_6H_5-P(O)$(OH)_2$ having a melting point of 161-162°C.

Polymeric materials were not found in this reaction. On the other hand, a polymer was produced when we reacted C_6H_5-PCl_2 with dimethyl sulfoxide in a mole ratio of 1:2 respectively. Tetrachloroethane was used as solvent in this reaction also. The reaction temperature was always kept below 70°C. After the reaction was completed and the solvent had been distilled off, a viscous residue was obtained which solidified on standing to a brittle, glassy mass which could be easily pulverized. Analysis of this material indicated a composition corresponding to



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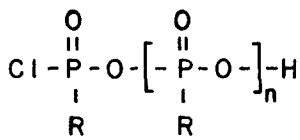
Thus, a substance is produced in which phosphorus atoms with coordination number four are interconnected by way of an oxygen bridge. In general, polymers having the following formula are obtained:



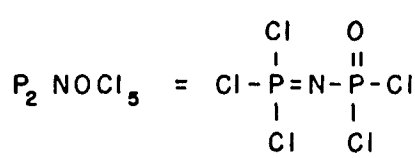
R = C_6H_5

n = 16 - 17

XXIX

This polymeric phenylphosphonic acid is stable up to 300°C. In the range 300 to 350°C it loses half its original weight. An oily residue then remains which consists of polymeric phosphoric acid $\left[HOP_3\right]_x$. These polymeric phosphoric acids vaporize at 500-600°C.

When we reacted diphenylchlorophosphine with dimethyl sulfoxide in a mole ratio of 1:1, we obtained $(C_6H_5)_2$P(O)Cl; with a corresponding ratio of 1:2 respectively, $(C_6H_5)_2$P(O)OH was produced. No polymeric substances were formed in these reactions. On the other hand, a polymer was obtained when we reacted P_2NOCl_5 (prepared earlier by us) with diphenyl sulfoxide.



The product of this reaction remained stable up to 75°C in a stream of nitrogen. Between 570 and 610°C 30-35 percent of the original weight was lost and a white residue remained which consisted of $(PNO)_n$.

XXX

This substance proved to be stable up to 900°C and was completely stable towards hydrolysis. It was insoluble in all common solvents.

SECTION VII

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4. Otto, R. J. A. and Audrieth, L. F., J. Am. Chem. Soc., 80, 5894 (1958).

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13. ABSTRACT

A variety of chemical systems containing phosphorus-nitrogen bonds have been investigated as potential intermediates for the synthesis of polymeric materials having extreme thermal and chemical stability. These investigations include: the preparation of various phosphorus nitride salts containing phenyl groups and the reactions of these compounds with diamines in order to produce phosphorus-nitrogen polymers, the preparation of various phosphorus nitride dichlorides in order to obtain suitable starting materials for isomer preparation and the reaction of known phosphorus nitride dichlorides in such a manner as to form six- and eight-membered ring systems containing phosphorus and nitrogen as ring components which would be linked by $N\text{-}SO_2\text{-}N$ bridges.

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	ROLE	WT	ROLE	WT	ROLE	WT
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